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PREPARATION FOR PRODUCING A MATERIAL USED TO RESTORE A MINERALISED SUBSTANCE, IN PARTICULAR IN THE DENTAL FIELD

This invention relates to a preparation for producing a material used to restore a mineralised substance, in particular in the dental field.

In the dental field, the crown is restored so as to overcome, inter alia, the loss of substance associated with the destruction of dental tissue by caries or resulting from a shock.

Until now, the restoration of "impaired" teeth accounts for 75 to 80 % of dental treatments (P. Hescot et al. ; 1996 ; Programme International de Recherche de l'Organisation Mondiale de la Santé sur les déterminants et la santé bucco-dentaire ; Association Dentaire Française).

Currently, dental restoration uses essentially two types of materials for restoration to avoid the need for involvement of a prosthesis laboratory.

The oldest material, used since the 19th Century, is silver amalgam.

Very widely used, its placement by the practitioner is very simple and its mechanical strength has long been demonstrated. Moreover, the average lifespan of an amalgam filling is estimated to be 14 years.

However, silver amalgam has two major disadvantages.

The first disadvantage is associated with the presence of 40 to 50 % mercury in its composition. The possible danger of the release of mercury in the saliva and the environment when positioning the material, as well as in wastewater when it is removed, has led to a gradual rejection of the use of this type of material.

The second disadvantage is associated with the inaesthetic metal appearance of fillings made with silver amalgam.

To overcome the disadvantages of the presence of mercury and the inaesthetic appearance of silver amalgams, a second type of restoration material has been developed. It consists of composite resins.

The composite resins are formed by a mixture of organic resin and mineral fillers, which is specifically treated with a product that ensures the binding of the resin to the mineral fillers, without any mercury.

Originally intended for the treatment of anterior teeth, because they satisfy the patients' aesthetic requirements, they are also used for the restoration of posterior teeth.

However, it is noted that the fillings produced with these composite resins have an estimated average lifespan of 7 years, that is half that of the silver amalgam fillings.

This short lifespan of composite resin fillings can be explained by the phenomenon of contraction of the composite resin which occurs during the setting reaction of the composite resins and which no longer provides an adequate marginal seal during the polymerisation reaction, which constitutes a major problem in the use of such resins.

Until now, and in spite of numerous attempts to improve the components of composite resins as well as the associated techniques for use, no composite resin has an adequate marginal seal, in particular in the areas where there is little or no enamel.

In addition, the environmental and aesthetic advantages of composite resins lead to lower spending in terms of public health and savings for the health care budget.

Therefore, there is a real need to have a restoration material for dental reconstitution that offers a compromise between the advantages of silver amalgams, in particular in terms of longevity and mechanical strength, and those of composite resins, namely the absence of mercury and the aesthetic appearance of the filling.

The objective of this invention is therefore to provide a material used to restore a mineralised substance, in particular for dental restoration, which is capable of resisting pressures of approximately at least 100 Mpa, which moreover has dimensional stability during its placement and after it, and finally has good adhesion to the mineral substance that it is intended to restore.

An additional objective of the invention, in particular in dental applications, is to produce a material having the aforementioned characteristics and which is moreover biocompatible.

Specifically in the dental field, this material must also provide a good marginal seal without any linear contraction so as to ensure an average lifespan approaching that of silver amalgams, provide an aesthetic filling, be resistant to chewing pressures within the pressure value range indicated above, and have a setting time compatible with the handling time necessary for the dental surgeon, i.e. 10 to 30 minutes.

According to the invention, a preparation for producing such a material includes

- an aqueous liquid part,

- a solid part containing at least one silicate selected from tricalcium silicate Ca_3SiO_5 and dicalcium silicate Ca_2SiO_4,

- calcium chloride $CaCl_2$ and a water-reducing agent, both contained in at least one of the aforementioned parts,

in which the solid part and the liquid part are intended to be mixed in order to obtain said material.

Thus, "solid part" refers to all of the solid phases, consisting of the powders of each of its constituents, and "liquid part" refers to the aqueous liquid phase in which the other constituents that make up this liquid part or phase can be added to water.

The water-reducing agent enables the amount of water to be reduced and thus the volume of the liquid phase to be adjusted with respect to that of the solid phase, without adversely affecting the hydration of the tricalcium silicate and/or the dicalcium silicate, which occurs during the mixture of the solid and liquid phases.

The water-reducing agent advantageously has a fluidifying and/or plasticizing capability.

Such properties of the water-reducing agent thus impart fluidity and plasticity on the material obtained after mixture of the preparation according to the invention, making it easier for the practitioner to mix and handle the material.

In particular, plasticizers can be used as water-reducing agents, such as, for example, polynaphthalene sulfonate (PNS) or a plasticizer, referred to as a "superplasticizer", based on modified polycarboxylate.

For dental restoration, the solid part further contains calcium carbonate $CaCO_3$.

Calcium carbonate has an accelerating effect on the hydration of calcium, dicalcium or tricalcium silicate.

Moreover, it enhances the properties of resistance to compression of the material obtained after mixing of the preparation according to the invention.

Preferably, in the dental field, the solid part contains between 70 % and 99 % by weight of dicalcium and/or tricalcium silicate, and between 1 and 30 % by weight of calcium carbonate $CaCO_3$, these weight percents being given on the basis of all of the constituents of the solid part.

The solid part preferably contains zirconium oxide Z_rO_2.

Zirconium oxide has two advantages.

With remarkable hardness, it further enhances the mechanical properties of the material obtained from the preparation according to the invention.

Moreover, by increasing the radio-opacity of this material, the practitioner has improved radiographic control for the restoration of the mineralized substance.

The proportion of zirconium oxide is preferably between 0 and 15 % by weight of all of the constituents of this solid part.

According to an embodiment relevant to all of the applications of the present invention, it is the liquid part that contains the $CaCl_2$.

The content of $CaCl_2$ can, for example, be between 1 and 35 %, and preferably between 9 and 25 %, by weight of the total volume of this liquid part.

In another embodiment, it is the solid part that contains the calcium chloride.

The calcium chloride content in the solid part can, for example, be between 0.1 and 10 % by weight of all of the constituents of the solid part, and preferably between 0.9 and 7.5 %.

The liquid part can contain the water-reducing agent.

The proportion of water-reducing agent in this liquid part is, for example, between 0.1 and 10 % by weight of the total volume of the liquid part, advantageously between 1 and 5 % by weight and preferably between 2 and 4 %.

In another embodiment, it is the solid part that contains the water-reducing agent.

The content of the water-reducing agent in the solid part is, for example, between 0.01 and 3 % by weight of all of the constituents of the solid part, advantageously between 0.15 and 1.25 % and preferably between 0.38 and 0.84 %.

Plasticizer-type water-reducing agents, such as those mentioned above, can be used in the liquid part or the solid part.

Regardless of the intended uses of the preparations according to the invention, the volume-to-mass ratio between the liquid part and the solid part may be between 0.1 and 0.3, advantageously between 0.15 and 0.25 and preferably between 0.17 and 0.23.

This ratio may vary in particular according to the choice of the water-reducing agent.

In an advantageous embodiment of the invention, the components of the solid part are micronised.

Preferably, an in particular for dental restoration, at least 90 % of the particles of each of the constituents of the solid part have a particle size of less than 10 μm.

The invention also relates to a method for making the preparation for producing a material used to restore a mineralised substance, in particular in the dental field, based on the preparation according to the invention.

According to the invention, the solid part and the liquid part are mixed using any means transmitting a high energy to said mixture.

After obtaining a uniform mixture of the two liquid and solid parts, a product with a whitish tint is obtained, which can then be easily implemented.

The material obtained according to the invention, which obviously does not contain mercury, is a more than 95 % mineral product, thereby ensuring excellent biocompatibility.

The invention also relates to the use of the preparation according to the invention to obtain a material for restoring teeth, an apical sealing cement, a dentino-cemental substitute, a cavity-lining material and a jawbone filling material.

The preparation according to the invention can specifically be used in the dental field according, inter alia, to the embodiments mentioned as follows, which enable all of the desired characteristics mentioned above to be obtained.

The material according to the invention is particularly promoted for the restoration of teeth, and

more specifically, but not limited to posterior teeth, molars and premolars.

It can also be used as an apical sealing cement, by the so-called "retrograde" surgical route or canal route, or as a dentino-cemental substitute in the case of iatrogenic or pathological canal or pulpal floor perforations, but also as a cavity lining with or without pulpal exposure.

The material according to the invention can also be used for filing the bones of the jaw.

Owing to its whitish colour, the dental material is entirely satisfactory with regard to the aesthetic requirement.

It is also entirely possible to consider including a colouring agent in the preparation, in its solid and/or liquid part, so as to increase the range of possible colours.

Thus, it becomes possible to prepare a dental material of which the final colour will perfectly match the colour of the patient's teeth.

Other properties and advantages of the invention, given as non-limiting examples in reference to the appended figures, are described below.

- Figure 1 is a reproduction of an image observed through a scanning electron microscope and showing the polished cross-section of a premolar cavity filled with cement prepared from the preparation according to the invention ; and

- Figure 2 is an enlarged reproduction of the area indicated with the white box in figure 1.

The material according to the invention used as a dental cement to restore the premolar, of which one part

is shown in figure 1, was prepared from the following preparation, in a liquid part/solid part mass ratio of 0.21 :

Solid part (for 100 g) :

Ca_3SiO_5	85 g
$CaCO_3$	15 g

Liquid part (for 100 ml) :

$CaCl_2$, $2H_2O$	14.7 g
water-reducing agent	3 g
water	q.s.f. 100 ml

The powdered raw materials of the solid part used are micronised at least for this dental use. Preferably and generally, their particle size is less than 10 microns.

In this example, the particle size characteristics of the various constituents are as follows :

- for Ca_3SiO_5 : $d_{10} = 0.81\ \mu m$

$d_{50} = 3.16\ \mu m$

$d_{90} = 7.51\ \mu m$

with d_x representing the maximum size reached by x% of the particles of the compound considered, in this case for Ca_3SiO_5.

- for $CaCO_3$, the average diameter of the particles is between 50 and 100 nm.

According to a different embodiment, the preparation according to the invention can contain zirconium oxide Z_rO_2.

Such a preparation can also constitute a dental cement, in particular for apical sealing uses, by the so-called "retrograde" surgical or canal route, for which a material with good radio-opacity is necessary.

Such a cement is prepared from the following preparation :

Solid part (for 100 g) :

Ca_3SiO_5	80.75 g
$CaCO_3$	14.25 g
Z_rO_2	5.00 g

Liquid part (for 100 ml) :

$CaCl_2$, $2H_2O$	14.7 g
water-reducing agent	3 g
water	q.s.f. 100 ml

the liquid part/solid part mass ratio in this case is 0.18.

In this second example, the particle size characteristics of Z_rO_2 are as follows :

$d_{10} = 0.28\ \mu m$

$d_{50} = 0.71\ \mu m$

$d_{90} = 1.53\ \mu m$

with d_x being defined as above and the particle size characteristics of the two other constituents Ca_3SiO_5 and $CaCO_3$ being identical to those of the previous example.

The water-reducing agent used in these two embodiments was a new generation plasticizer, called a "superplasticizer", based on modified polycarboxylate sold by the Chryso company under the trade name "Chrysofluid Premia".

The practitioner extemporaneously mixes the solid and liquid parts then places the dental material obtained, for example with an amalgam carrier, for the dental work to be carried out.

In this case, after mixing one of the preparations discussed in the examples above, the cement was inserted

into a premolar cavity, using the conventional tools of the practitioner.

In the aforementioned examples, the preparations discussed were mixed using an automatic mixing means transmitting to the preparations a high energy so as to obtain a uniform paste that can then be placed using an amalgam carrier.

The setting time of the material in the dental application according to the invention is compatible with the handling time of the practitioner, and is obtained without the intervention or addition of any substance : this setting indeed occurs without any photo- or chemically-polymerizable monomer additive and without the use of ultrasound as is the case with the current resins.

Under conditions of use at 100 % moisture and 37° Celsius, a dental material is obtained having all of the desired characteristics, such as :

- no shrinkage over time, with perfect dimensional stability,
- resistance to compression within 24 hours of 100 to 200 Mpa,
- good adhesion to the dental tissue as shown in the appended figures,
- acceptable aesthetic appearance,
- non-solubility after setting,
- electrical and thermal insulation,
- hardness suitable for chewing, and
- simple and practical clinical handling of the preparation, and thus of the material obtained after mixing this preparation.

In figure 1, the dentin is identified at the level of its interface with the cavity of the premolar.

This cavity is filled with the material, or dental cement, according to the invention. At the level of the dentin, a dentinal tubule appears, of which one part is indicated with a white box.

In figure 2, the expansion of the box shows in detail the inside of the dentinal tubule. It is noted that this interior is characterized by the presence of a large number of crystals.

An analysis of these crystals has shown that they consist of silicon, which must come from the dental cement inserted into the premolar cavity.

This means that the dental material thus used remarkably fills not only the entire cavity of the tooth, but also that it penetrates the inside of the dentinal tubules passing through the dentin.

Thus, by creating physicochemical bonds with the mineralised tissues, and in particular the dentin, the dental cement enables a good marginal seal to be obtained.

This good marginal seal is reinforced by the fact that the dental cement maintains its dimensional stability : indeed, no linear contraction has been observed.

Moreover, this dental cement has the mechanical properties necessary for a material for filling teeth, in particular posterior teeth, and is probably of a durability greater than composite resins.

Furthermore, the material obtained from the preparation according to the invention is not cytotoxic, and is therefore particularly beneficial.

The evaluation of cytotoxicity, and therefore the possible toxic activity of the cement on certain cells leading to their destruction, has been conducted

according to the AFNOR protocol, standard S 99-505-5, NF EN, ISO 10 993-5 of December 1999.

The cellular mortality rate observed at three different times – 3 hours, 1 day and 7 days, respectively, after the setting of the cement, was in all three cases lower than 10 %, which corresponds to zero toxicity according to this AFNOR standard.

Although this describes more specifically a preparation for dental restoration, it relates more generally to a material for restoring a mineralised substance, without any restriction on the scope of the invention.

Such a material can thus be used as an apical sealing material, by the so-called "retrograde" surgical or canal route, as a dental cement substitute, in the case of iatrogenic or pathological canal or pulpal floor perforations, as a cavity lining with or without pulpal exposure, or as a filling material for jaw bones.